

# Validation of SAGE-III Measurements of NO<sub>3</sub>: Ground-Based Vertical Profile Measurements

Status Report for the EOS Validation Program  
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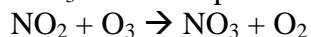
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## Goals of the Investigation

The SAGE III Science Team has established requirements for validation studies to assess the precision and accuracy of the SAGE III measurements of O<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>O, NO<sub>3</sub>, OCIO and other trace species. The work described in this report is aimed at providing ground-based vertical profile and column measurements of NO<sub>3</sub> and NO<sub>2</sub> using the same methodology as the actual SAGE III technique, i.e. lunar and solar occultation in the UV/visible spectral region. Spectra are recorded using two different instruments: a 0.05 cm<sup>-1</sup> interferometer (FTUVS) and a grating spectrograph which utilizes a diode array detector. Both instruments are located at the Table Mountain Facility of the Jet Propulsion Laboratory. Measurements are compared with results from the Caltech/JPL 1-d model to validate mechanisms of stratospheric NO<sub>x</sub> chemistry.

## Background

Interest in measurements of NO<sub>3</sub> stems from its role as a radical intermediate in the nighttime conversion of NO<sub>x</sub> to NO<sub>y</sub>. NO<sub>3</sub> is formed primarily in the reaction



and removed by the reaction



The significance of this sequence lies in the fact that N<sub>2</sub>O<sub>5</sub> is the anhydride of nitric acid, HNO<sub>3</sub>, which is an important temporary reservoir of NO<sub>x</sub> in the lower stratosphere. The conversion of N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> in the stratosphere occurs on the surface of stratospheric sulfate aerosol (SSA) with high efficiency. The rate-limiting process in the conversion of NO<sub>x</sub> to HNO<sub>3</sub> through these reactions is the NO<sub>2</sub> + O<sub>3</sub> reaction when the SSA surface area is elevated above background conditions. Under background conditions, or at altitudes that lie above the peak in the SSA vertical profile, the conversion rate is limited by the available aerosol surface area. Simultaneous measurements of NO<sub>2</sub>, NO<sub>3</sub> and aerosol surface area are therefore key parameters in the understanding of the NO<sub>x</sub> budget. Since NO<sub>x</sub> plays an important role in the catalytic destruction of O<sub>3</sub> in the lower stratosphere, these measurements are crucial to the understanding of long-term trends in O<sub>3</sub>.

Rapid photochemical destruction of NO<sub>3</sub> results in daytime mixing ratios that are extremely small. After sunset, however, this loss mechanism disappears causing NO<sub>3</sub> mixing ratios to increase rapidly. Lunar occultation is therefore an excellent method for the measurement of NO<sub>3</sub> using the technique of long-path visible absorption spectroscopy. While this technique has not yet been used from a satellite platform, it has been employed successfully from balloon and ground-based sensors. The method takes advantage of the intense NO<sub>3</sub> (0,0) absorption band at 662 nm and another strong feature at 623 nm. The spectrum of NO<sub>3</sub> in this spectral region is well established from laboratory studies down to temperatures around 220 K. The spectroscopic

determination of NO<sub>3</sub> is affected by interferences from the O<sub>2</sub>  $b^1_g(v=2) \rightarrow X^3_g(v=0)$  band at 625 nm and a moderately strong water vapor band in the 640-665 nm spectral region. Despite its large cross sections at band peaks, the absorption features of NO<sub>3</sub> are quite weak with slant optical depths ranging from 0.01% to about 1% through the nighttime viewing period.

### Methodology

With support from the EOS Validation Program, we have developed a measurement capability for NO<sub>3</sub> to provide correlative measurements for SAGE III and other future spaceborne UV-visible sensors including SCIAMACHY and OMI. The approach involves the use of a high resolution (0.05 cm<sup>-1</sup>) Fourier Transform spectrometer (FTUVS) and a medium resolution grating spectrograph which incorporates a 1024-channel diode array detector. Both instruments operate in the UV-visible-NIR spectral region (0.29-1.1 μm). The foreoptics for both instruments consists of a 32 in. dia. heliostat feeding an 8 in. off-axis telescope with f/3 optics. The telescope has dual collimating mirrors, one feeding the spectrometers and the other providing an image to a tracking camera for fine guidance of the heliostat. This capability permits the spectrometers to be pointed at specific features on the solar and lunar disks which is useful in a number of applications.

### Progress

#### *Algorithm Development*

As discussed in previous reports, processing of lunar spectra to obtain the NO<sub>3</sub> column abundance consists of several steps including dark noise subtraction, wavelength calibration using line spectra from a neon emission lamp, ratioing of the spectra with a reference spectrum taken before appreciable buildup of NO<sub>3</sub>, and fitting of the resulting absorption spectra using reference spectra for NO<sub>3</sub> and other species including H<sub>2</sub>O, O<sub>2</sub>, O<sub>3</sub>, etc. In the past year, progress has continued on the development of an automated retrieval procedure that follows the above steps. It was found that a significant reduction in the residuals could be obtained by low-pass filtering the reference spectrum. This procedure recovers slowly varying spectral components such as the variation with wavelength of the grating efficiency and detector responsivity. Subtraction of these terms considerably improves the spectral fits for NO<sub>3</sub>.

#### *Measurements of NO<sub>3</sub>*

With the current approach, NO<sub>3</sub> spectra are obtained using the Moon as a light source when the lunar phase is within two days of full. This requirement arises both from the sharp dependence of lunar intensity on lunar phase, and from the need to match the temporal dependence of NO<sub>3</sub> with the availability of the Moon as a target. The number of viewing opportunities is further limited by clouds. Since the last progress report (May, 2000), good lunar spectra were obtained on the following 18 days:

6/15/00	8/22/00	4/9/01
6/16/00	8/23/00	5/6/01
6/17/00	8/24/00	5/7/01
6/18/00	8/25/00	8/2/01
8/13/00	4/7/01	8/3/01
8/14/00	4/8/01	8/4/01

There was a significant measurement gap between September, 2000 and April, 2001 due to the sudden departure of a key postdoctoral associate, and the inability to find a replacement on short notice. The project is currently fully staffed and NO<sub>3</sub> measurements will be made on every available opportunity.

#### *NO<sub>3</sub> Measurements Using Stellar/Planetary Objects*

The use of the Moon as a light source restricts the number of opportunities to measure the entire nighttime variation of the NO<sub>3</sub> column abundance to three or four nights per month. This limitation arises for two reasons. First, only near full Moon is the lunar ephemeris meet the requirements for optimal NO<sub>3</sub> retrievals, i.e. high geometrical air mass factor near sunrise to record the dependence of the NO<sub>3</sub> column abundance on solar radiance. Second, the lunar brightness sharply maximizes near full moon, minimizing the required integration time. Although the nighttime measurements of SAGE III will also be made near full moon, it would be desirable to have the capability of recording NO<sub>3</sub> spectra without being restricted by the lunar ephemeris.

To address this problem, studies were carried out this year using astronomical light sources other than the Moon. Because stars and planets are effectively point sources, in contrast to the Moon which is an extended object, effective use can be made of large astronomical telescopes to improve the measurement SNR. For this study we used the 0.6 m reflector at Table Mountain Observatory. This telescope has a Coudé focus which normally feeds a high resolution grating spectrograph. For our experiments the light from the Coudé focus was coupled to the 0.3 m spectrometer/diode array system using foreoptics which matched the f/number of spectrometer.

The initial experiments used the bright objects Vega and Jupiter. While spectra were of sufficient quality to provide good measurements of H<sub>2</sub>O and O<sub>2</sub> which have strong absorption features, the telescope aperture size was insufficient to obtain good NO<sub>3</sub> spectra using the existing detector. It may be possible to obtain better results with an intensified focal plane array such as an ICCD. Alternatively a larger telescope could be used. These options will be considered for future study.

#### *High Resolution Laboratory Spectroscopy of NO<sub>2</sub>*

The FTUVS instrument will be used in support of SAGE III and EOS Aura/OMI measurements of NO<sub>2</sub> by carrying out ground-based solar absorption measurements in the UV-visible region at high spectral resolution (0.05 cm<sup>-1</sup>). The NO<sub>2</sub> spectrum in the 400-500 nm region exhibits a very large number of narrow absorption features superimposed on a continuum. Preliminary spectroscopic work has shown that these features are very sensitive to both pressure and temperature in the ranges of atmospheric interest. This offers the possibility of using ground-based spectroscopy to determine the NO<sub>2</sub> profile through an analysis of atmospheric NO<sub>2</sub>

lineshapes. The spectroscopic data required to carry out these retrievals have not been yet been obtained, however.

To address this need, NO<sub>2</sub> spectra were obtained in July, 2001 using the Fourier Transform Spectrometer (FTS) at the McMath-Pierce Telescope which is part of the Kitt Peak National Observatory. The objectives of this work were to measure NO<sub>2</sub> cross sections in the 400-500 nm region with an accuracy of 5% or better, and to characterize the pressure broadening of NO<sub>2</sub> features at a spectral resolution of 0.05 cm<sup>-1</sup> over the applicable atmospheric pressure/temperature range. The McMath-Pierce FTS is the premier spectrometer for this type of measurement.

The spectra are currently being analyzed but preliminary results indicate that the spectra have high signal-to-noise ratios and good baseline stability. Calibrations are being carried to assess the accuracy of the system that quantified NO<sub>2</sub> in the spectroscopic cell. Following analysis, the spectra will be published in the refereed literature and made available to interested users on an ftp site.

### Planned Activities

The activities for the coming year may be summarized as follows:

#### *NO<sub>3</sub> Measurements*

1. Improvements to the NO<sub>3</sub> spectrograph will be implemented including active temperature control of the spectrograph housing, active pumping of the detector head to permit operation at lower temperatures, and development of a new telescope for portable operation of the spectrograph.
2. NO<sub>3</sub> measurements will be carried out at every full moon viewing opportunity, weather permitting.
3. Carry out a site survey for deployment of the portable instrument at the Mt. Barcroft Laboratory (12,249 ft MSL) operated by the University of California White Mountain Research Station.
4. Coordinate plans for validation measurements with the SAGE III Science Team.

#### *NO<sub>2</sub> Measurements*

1. Analyze and publish the high resolution NO<sub>2</sub> spectra obtained using the McMath-Pierce FTS.
2. Continue work on the retrieval algorithm for NO<sub>2</sub> retrievals using FTUVS spectra taken at 0.05 cm<sup>-1</sup> resolution. This will include an analysis of the feasibility of coarse vertical profile retrievals from daytime solar absorption spectra.

#### *Modeling*

1. The JPL/Caltech 1-d atmospheric model will be used in the analysis of NO<sub>2</sub> and NO<sub>3</sub> measurements from FTUVS and the spectrograph. Comparisons will be made between measurements and model calculations of the NO<sub>3</sub> column constrained by measurements of NO<sub>2</sub> from the spectrograph, the O<sub>3</sub> vmr from the DIAL system at TMF, NCEP temperature profiles and other relevant trace species measurements from UARS and other spacecraft. The results will be used to assess the adequacy of existing models of stratospheric NO<sub>x</sub> chemistry.

## Schedule

Tasks are referenced to the numerical levels in the previous paragraphs

<b>Task/ Month</b>	<b>Aug 2001</b>	<b>Sept</b>	<b>Oct</b>	<b>Nov</b>	<b>Dec</b>	<b>Jan 2002</b>	<b>Feb</b>	<b>Mar</b>	<b>Apr</b>	<b>May</b>	<b>Jun</b>	<b>July</b>
<b>NO<sub>3</sub></b>												
<b>1</b>												
<b>2</b>												
<b>3</b>												
<b>4</b>												
<b>NO<sub>2</sub></b>												
<b>1</b>												
<b>2</b>												
<b>Models</b>												
<b>1</b>												

### Collaboration with the SAGE III Instrument Team:

There are several areas of mutual interest between our group and the SAGE III Instrument Team including:

- comparison of retrieval algorithms for NO<sub>3</sub> and other species using lunar spectra
- treatment of interfering spectral features
- use of a common spectroscopic database for NO<sub>3</sub> and other molecules
- methods for the comparison of SAGE III vertical profiles with the column and profile data obtained from ground-based sensors
- separation of the NO<sub>3</sub> contributions from the stratosphere and troposphere, especially where regional NO<sub>x</sub> sources are important

The PI of this task will attend SAGE III Science Team meetings if invited by the SAGE PI.

Exchange of Correlative Data with Instrument Team and Other Investigators: It is our intention to disseminate the correlative data from this investigation to the Instrument Team as quickly as possible. While a protocol for this exchange has not yet been established, this will be accomplished well in advance of the SAGE III launch. Data from the correlative measurements will be available on our ftp site for rapid dissemination to interested users.